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High-pressure phase of the cubic spinel NiMn_2O_4

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It has been observed that the fcc spinel NiMn_2O_4 transforms to a tetragonal structure at about 12 GPa. The tetragonal phase does not revert to the cubic phase upon decompression and its unit-cell constants at ambient pressure are $a_0 = 8.65(8)$ and $c_0 = 7.88(15)$ Å (distorted fcc). Within the experimental uncertainty, there is no volume change at the transition. The c/a ratio of the tetragonal spinel is almost independent of pressure and equal to 0.91. The phase transition is attributed to the Jahn-Teller-type distortion and the ionic configuration can be assumed as $(\text{Mn}^{3+})_{\text{tet}}[\text{Ni}^{2+}\text{Mn}^{3+}]_{\text{oct}}$. The bulk modulus of the cubic phase is 206(4) GPa. [S0163-1829(98)01409-X]

INTRODUCTION

A considerable effort has been devoted to understanding the physical properties of the 3d transition-metal oxides, in particular those of the spinel type. The distribution and valencies of the metal ions in the spinels are of great importance for the interpretation of the magnetic, electric, and crystallographic properties of these materials.

NiMn_2O_4 is ferrimagnetic at low temperatures. Its negative temperature coefficient of resistivity has been found useful in electronic applications. The conditions determining the valency and the lattice site preferences of the two cations have been broadly discussed in the literature (see Åsbrink *et al.*¹ and Refs. 1–7 therein), but still they remain uncertain. Experiments have shown that the stoichiometry may strongly depend on the methods of preparation, i.e., on the temperature of synthesis and the annealing rate. These factors also determine the lattice constants and even the crystal system. Thus NiMn_2O_4 is cubic when prepared above about 1000 K and tetragonal² with $c/a > 1$ when the synthesis takes place at the lower temperature 473 K. In certain cases the crystal symmetry of spinels can give information about the valency states present. The distortion of the cubic symmetry can be detected for ions with octahedral coordination and electron configuration d^4 or d^9 . Thus a possible tetragonal distortion can be used to identify these ions.³

Recently, temperature-dependent magnetic, calorimetric, and single-crystal x-ray-diffraction investigations of stoichiometric NiMn_2O_4 were reported by Åsbrink *et al.*¹ A phase transition of purely magnetic nature was established at $T_c = 145$ K with the cubic crystal structure persisting below T_c .

Although both nickel and manganese ions can adopt more than one valence state, a detailed structure analysis suggested

a cation configuration where all the nickel ions are in the Ni^{2+} state and the manganese ions in the Mn^{2+} , Mn^{3+} , and Mn^{4+} states. Thus the formula is $(\text{Ni}_{1-x}^{2+}\text{Mn}_x^{2+})[\text{Ni}_x^{2+}\text{Mn}_{2(1-x)}^{3+}\text{Mn}_x^{4+}]\text{O}_4$, with $x = 0.80(1)$ at ambient temperature, and $x = 0.87(1)$ at 115 K. The observed magnetic moment per formula unit is $\mu_{\text{eff}} = 6.9\mu_B$. This value indicates that the magnetic interaction between the tetrahedral *A* and the octahedral *B* sites dominates over the *A-A* and *B-B* interactions. The manganese cations take part in this antiferromagnetic coupling which involves an electron exchange $\text{Mn}_A^{3+}-\text{O}^{2-}-\text{Mn}_B^{3+} \rightarrow \text{Mn}_A^{2+}-\text{O}^{2-}-\text{Mn}_B^{4+}$. Besides, the existence of Mn in two different valence states at the octahedral sites explains the electrical conductivity⁴ as well as the absence of the Jahn-Teller tetragonal distortion, which only can take place if the Mn^{3+} (d^4) part of the octahedral cations exceeds the critical value 0.52.⁵

The present experiment is an extension of our previous work¹ into the high-pressure regime. The aim has been to study the structural stability of NiMn_2O_4 under high pressure. The tetragonal phase obtained by de Vidales *et al.*² by way of synthesis at 473 K in the system $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ does not seem to be a direct transformation from the prototype cubic phase by just lowering the temperature. This tetragonal phase has a density of mass 6.6% lower than the density of the cubic phase, and therefore it cannot be supposed to form at high pressure. However, the low-temperature study of Åsbrink *et al.*³ shows that the inversion parameter increases from 0.80 at room temperature to 0.87 at 115 K. The parallelity between the effects of lowering the temperature and increasing the pressure suggests the possibility of further increasing the Mn occupation at the tetragonal sites by using high pressure, thereby inducing a transition to another tetrag-

onal phase. The results of the present work will be discussed in view of the presence of the Jahn-Teller active Mn^{3+} cations.

EXPERIMENTAL PROCEDURE

The NiMn_2O_4 sample used in this work was obtained from powdered single crystals. The latter were prepared by prolonged heating of equimolar mixtures of NiO and Mn_2O_3 in a sealed and evacuated silica tube, kept at the temperature 1323 K for 45 days and subsequently quenched in water. This method provides the high-temperature modification of NiMn_2O_4 with stoichiometric composition.¹

X-ray powder-diffraction spectra were recorded using synchrotron radiation and the white-beam energy-dispersive method. The experiments were performed at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) using radiation in the 15–70 keV photon energy range from a bending magnet. The diffractometer, working in the energy-dispersive mode, has been described elsewhere.⁶ High pressures in the range 0–60 GPa were obtained in a Syassen-Holzapfel-type diamond-anvil cell.⁷ The sample and a small ruby chip were enclosed in a small hole of diameter 0.1 mm in an Inconel gasket. A 4:1 methanol:ethanol mixture was used as the pressure-transmitting medium. The pressure was determined by measuring the wavelength shift of the ruby line and applying the nonlinear pressure scale of Mao *et al.*⁸ The uncertainty in the pressure determination is estimated to be 0.1 GPa for pressures lower than 10 GPa. For higher pressures the uncertainty may be larger because of nonhydrostatic conditions. The Bragg angle associated with each experimental run was deduced from a zero-pressure diffraction spectrum of rocksalt (NaCl) with a known lattice constant.

RESULTS AND DISCUSSION

The cubic spinel NiMn_2O_4 belongs to the space group $Fd3m$. Previous determinations of the lattice constant include Larson *et al.*⁵ 8.396(1) Å, Boucher⁹ 8.4028(3), and Renault *et al.*¹⁰ 8.400 Å. More references can be found in Åsbrink *et al.*,¹ who have obtained $a_0 = 8.379(1)$ Å and $V_0 = 588.27(2)$ Å³ in their single-crystal study at 115 K. We have used $a_0 = 8.390(15)$ Å as determined from an *in situ* zero-pressure diffraction spectrum. New diffraction lines appear at pressures about 12 GPa indicating a structural phase transformation. There is a considerable hysteresis in the transformation, and upon decompression the sample does not revert to the cubic phase. Thus it has been possible to determine the lattice constants of the high-pressure phase at ambient conditions, as will be discussed below.

The diffraction spectra of the high-pressure phase have been indexed according to a tetragonal distortion of the fcc unit cell; cf. Gerward *et al.*¹¹ Inspection of the 311/113 doublet indicates a c/a ratio less than one. In the tetragonal system the 311 line is about twice as strong as the 113 line, mainly because of the multiplicity factor. For $c/a < 1$ the 311 line occurs at a lower energy than the 113 line, i.e., $d_{311} > d_{113}$, in accordance with the observed diffraction spectrum (Fig. 1). The lattice constant a_c of the cubic phase as well as a and c of the tetragonal phase are shown as functions of

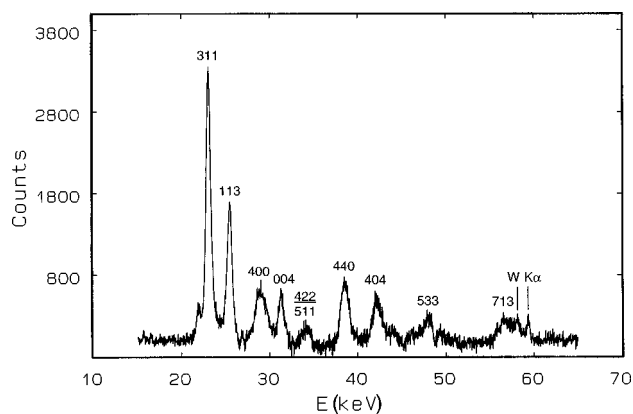


FIG. 1. Indexed energy-dispersive diffraction spectrum of tetragonal NiMn_2O_4 at 38.1 GPa; lattice constants $a = 8.35(10)$ and $c = 7.49(15)$ Å; Bragg angle $\theta = 6.045^\circ$. The peak on the left-hand side of the 311 reflection is due to fluorescence in the detector contact material (Ag).

pressure in Fig. 2.

The experimental pressure-volume data for the cubic spinel NiMn_2O_4 are given in Table I. The data have been described by the Birch equation of state¹² in the pressure range $P < 11$ GPa, thus avoiding possible problems with nonhydrostatic pressures for $P > 12$ GPa. The equation of state can be written

$$\frac{P}{B_0} = \frac{3}{2} (x^7 - x^5) \left[1 + \frac{3}{4} (B'_0 - 4)(x^2 - 1) \right],$$

where $x = a_0/a$, a being the lattice constant at pressure P and a_0 the zero-pressure lattice constant. The parameter B_0 is the bulk modulus and B'_0 its pressure derivative, both parameters being evaluated at zero pressure. The scatter of the data points did not allow the use of B'_0 as a fitting parameter. Instead, it was assumed that the pressure derivative is 4.00, which is a typical value for most solids. We obtain $B_0 = 206(4)$ GPa, where the estimated error within parenthesis

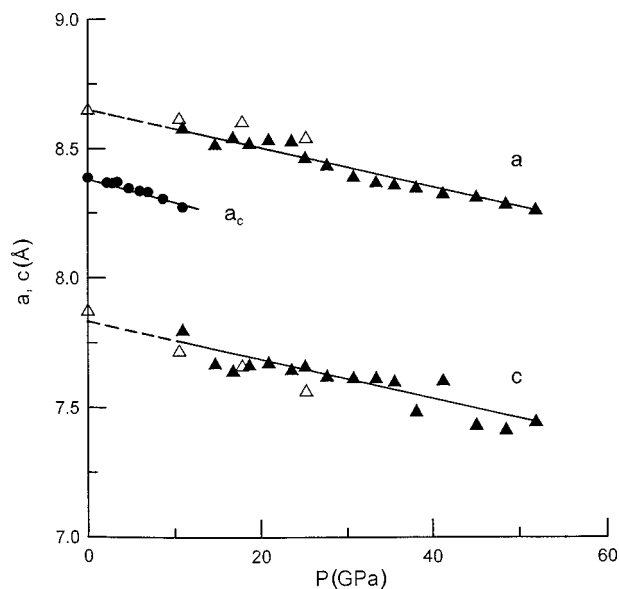


FIG. 2. Lattice constants for the cubic phase (a_c) and the tetragonal phase (a and c) as functions of pressure.

TABLE I. Compressibility data for cubic NiMn_2O_4 for $P < 11$ GPa. A fit of the Birch equation of state to the experimental data gives $B_0 = 206(4)$ GPa and $B'_0 = 4.00$ (see text).

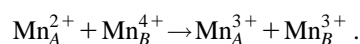
P (GPa)	a_c (Å)
0.00(10)	8.390(15)
2.21(10)	8.362(15)
2.91(10)	8.349(11)
3.41(10)	8.346(12)
4.72(10)	8.326(15)
6.04(10)	8.315(15)
6.95(10)	8.310(15)
8.68(10)	8.283(20)
10.92(10)	8.252(20)

is the standard error of the fit. To the best knowledge of the authors there are no data in the literature to compare the present value with. It may be mentioned that the bulk modulus of the mineral spinel (MgAl_2O_4) is 196 GPa, i.e., about the same value as the one found here for NiMn_2O_4 .

The tetragonal high-pressure phase does not revert to the cubic phase upon decompression. The lattice constants at ambient pressure are $a_0 = 8.65(8)$ Å and $c_0 = 7.88(15)$ Å, giving the unit-cell volume $V_0 = 589.6(20)$ Å³. The latter value agrees with the corresponding value for the volume of the fcc unit cell to within 0.2%. Given the experimental uncertainty, it has not been possible, in the present work, to determine any volume difference between the cubic and the tetragonal phases. The c/a ratio for the tetragonal phase is 0.91(2) at zero pressure, and the ratio is found to be practically independent of pressure. It may be noted that the high-pressure phase of NiMn_2O_4 is isostructural with the tetragonal Cr_2CuO_4 spinel,¹³ which has a c/a ratio of 0.92.

The existence of two different tetragonal phases of NiMn_2O_4 , one with $c/a > 1$ (de Vidale *et al.*²) and another

with $c/a < 1$ (present work) is interesting. In the former phase the inversion parameter is assumed to be approximately zero, and the tetragonal structure with $c/a > 1$ is a result partly of the octahedral distortion (elongation) caused by Mn^{3+} acting as an octahedral Jahn-Teller ion, and partly of the tetrahedral elongation caused by Ni^{2+} acting as a tetrahedral Jahn-Teller ion. In the present work we have not been able to determine positional parameters and we have no direct evidence of the cation distribution. However, some qualitative estimates can be derived from the results of Åsbrink *et al.*,¹ where the inversion parameter was found to increase with decreasing temperature. Thus we assume that, at sufficiently high pressure, the inversion parameter is approximately equal to one, and that the tetragonality ($c/a < 1$) is a result of the distortion (flattening) caused by Mn^{3+} , now acting as a tetrahedral Jahn-Teller ion. The Mn^{3+} ions are assumed to be formed by the superexchange interaction



The proposed cation distribution is therefore given by the formula $(\text{Mn}^{3+})[\text{Mn}^{3+}\text{Ni}^{2+}]\text{O}_4$. The observed hysteresis of the cubic to tetragonal transition can be explained by the existence of a potential energy barrier, hampering the electron exchange between the Mn cations in the tetrahedral and octahedral sites. Thus the tetragonal phase can be quenched to atmospheric pressure.

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